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A natural analogue study of CO_2-cement interaction: carbonate alteration of calcium silicate hydrate-bearing rocks from Northern Ireland

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A natural analogue study of CO_2-cement interaction: carbonate alteration of calcium silicate hydrate-bearing rocks from Northern Ireland

A.E. Milodowski, A Lacinska and D Wagner

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Scawt Hill, Co. Antrim, Northern Ireland.

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JRAP-14: Reactions between CO_2 and borehole infrastructure

DELIVERABLE JRAP-14/2:

A natural analogue study of CO_2-cement interaction: carbonate alteration of calcium silicate hydrate-bearing rocks from Northern Ireland

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JRAP-14 CO-ORDINATOR: K. Bateman BGS
kba@bgs.ac.uk

LEAD NoE PARTNER FOR THIS DELIVERABLE: A.E Milodowski,
aem@bgs.ac.uk

NoE PARTNERS INVOLVED FOR THIS DELIVERABLE:

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Foreword

The underground sequestration of anthropogenic carbon dioxide (CO_2) is one potential methodology for reducing our emissions of this greenhouse gas into the atmosphere, and hence reducing a driver for climate change. For this technique to be effective, the CO_2 must remain underground for timescales measurable in thousands of years or more. A key factor in such long-term containment is the efficacy of the seals overlying the stored CO_2. Boreholes penetrating potential CO_2 storage aquifer/reservoir formations provide potential pathways for CO_2 leakage that may cross formations and breach overlying seals strata. In this respect, understanding the long-term stability of cement and steel casing used in borehole completion and sealing, and their interaction with CO_2 are of paramount importance.

The focus of this report is to provide an insight into the long-term stability of borehole cement and its potential interactions with CO_2 from studying the alteration, through carbonation, of naturally-occurring cementitious calcium silicate and calcium silicate hydrate (CSH) materials in natural systems (i.e. “natural analogues”). These natural analogues observations may provide information on processes and reactions that may affect the long-term stability of borehole cements over greater timescales than can be studied in laboratory experiments (which are limited by reaction kinetics and may be influenced by the formation of metastable phases).

Acknowledgements

The authors thank Ian Mitchell of the Geological Survey of Northern Ireland, Department of Enterprise, Trade & Investment, for providing logistics support and geological guidance during fieldwork in Northern Ireland. The European Commission (EC) is gratefully acknowledged for its co-funding of this work (under EC project SES6-CT-2004-502816).

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Capture and storage of CO_2 underground in depleted hydrocarbon reservoirs and deep saline aquifers for thousands of years is being considered as one method to reduce emissions of CO_2 to the atmosphere in order to combat global warming. However, if CO_2 sequestration is to be a practicable large-scale disposal method, there is a need to ensure that it will remain safely underground, and not return rapidly to the atmosphere within relatively short timescales (e.g. a few thousands of years). One of the potential leakage routes for CO_2 is via wells drilled into the reservoir or aquifer, either during the exploitation of the reservoir or for CO_2 injection. The majority of well completions in oil and gas fields are based on the deployment of Portland-type cements. However, the Portland cement type materials used in hydrocarbon wells and water boreholes are susceptible to reaction with CO_2. The carbonation reactions between the hydrated (and residual unhydrated cement clinker) Portland cement components and CO_2 are thermodynamically favourable, and produce carbonate and bicarbonates that potentially may leach from the cement matrix, thereby increasing porosity and permeability and decreasing compressive strength. The operational design life expectancy of a typical oil well does not usually exceed 25-30 years. However, efficient borehole sealing for CO_2 sequestration requires a considerably longer lifetime, measurable in hundreds or thousands of years. It is very important therefore to understand the behaviour of borehole materials in the longer term. Observations of natural analogues of cement minerals may therefore provide valuable information on the long-term (thousands of years) stability and behaviour of cements.

Natural analogues in which either groundwater chemistry and/or mineral systems are similar to those encountered in man-made Portland cement systems are very rare, and are known from only a small number of restricted geological environments. The JRAP-14 research project examined sites from County Antrim, Northern Ireland, where natural cement clinker minerals and their secondary hydration products have previously been described from contact metamorphic aureoles and skarns around Tertiary dolerite plugs intruded into Upper Cretaceous chert (flint)–bearing Ulster White Limestone Formation. A field visit was undertaken in July 2007 to examine and sample the metamorphic aureoles around four dolerite plugs at Scawt Hill, Carneal Plug, Ballycraigy Plug and Ballygalley in County Antrim, Northern Ireland.

Fifteen samples of natural analogue material were successfully collected for detailed mineralogical investigations from two of the sites: Scawt Hill and Carneal Plug. The bulk mineralogical characteristics of the altered hornfelsed flints and metasomatised limestone samples were analysed using X-ray diffraction (XRD) analysis, Optical petrography, and backscattered scanning electron microscopy (BSEM) coupled with semi-quantitative energy-dispersive X-ray microanalysis (EDXA), were also carried out to characterise the hydration and carbonation fabrics.

High-temperature contact metamorphism of diagenetic silica concretions (chert or flint) within the Ulster White Limestone Formation at Carneal Plug and Scawt Hill has produced a hornfelsed rock comprising primary metamorphic assemblage dominated of larnite (α-Ca_2SiO_4), sometimes accompanied by wollastonite ($CaSiO_3$), spurrite ($Ca_5(SiO_4)_2(CO_3)$, paraspurrite ($Ca_5(SiO_4)_2(CO_3)$, brownmillerite ($Ca_2(Al,Fe)_2O_5$), quartz (SiO_2), calcite ($CaCO_3$). Magnetite (Fe_3O_4) and andradite-grossular garnet are also significant minerals. Hydroxylapatite is present as a minor component in some of the samples from Scawt Hill. The cores of well-preserved hornfelsed chert from Scawt Hill are predominantly composed of fine crystalline intergrowth of larnite. However, in larger hornfelsed flint nodules may have cores of fine to coarsely crystalline quartz, grading outwards into larnite-quartz rock and eventually larnite sometimes accompanied by minor bredigite. Spurrite and paraspurrite occur as well-crystallised minerals, intergrown with larnite, in the outer part of these hornfelsed flints, adjacent to the marble host rock. These carbonate minerals appear to be part of the original high-temperature metamorphic assemblage,

probably forming by recarbonation of the calcium silicate rock at high temperature as metamorphism waned. The strongly metasomatised rocks from Carneal plug have a more complex mineralogy, with hornfelsed chert containing a crystalline intergrowth of quartz, larnite, brownmillerite, and wollastonite, enclosed within a matrix of metasomatised marble containing pyroxene, andradite-grossular garnet, titanite (sphene) and magnetite.

The larnite nodules usually display significant alteration as a result of hydration and reaction with groundwater or as a result of exposure to weathering. The alteration may form reaction rims around the margins of a residual core containing relicts of larnite. In the case of Scawt Hill, even larnite nodules freshly exposed by splitting large blocks of recently fallen marble often showed evidence of extensive alteration and hydration, with the replacement of larnite by a very soft, moist, CSH gel. XRD and BSEM identified the CSH gel hydration products of the larnite as tobermorite (11 Å and 14Å variants) and amorphous CSH gel.

Carbonation of the CSH hydration rim is evident in most of the samples examined. It proceeds progressively from the outer margins and then along microfractures developed at the interface between the marble host rock and hydrated alteration rim around the larnite nodules. The reaction produces a dense low porosity rock within the calcite-scawtite-larnite rim around the nodules of the margins. This alteration is accompanied by shrinkage of the underlying altering CSH gel creating microfractures along which further reaction and carbonation occurs. The CSH gel and tobermorite are replaced by very fine grained groundmass of calcium carbonate. Petrographically, it was not possible to differentiate the carbonate minerals in this fine grained alteration. However, XRD analysis identifies this carbonated material to comprise a mixture of mainly calcite and scawtite ($Ca_7Si_6(CO_3)O_{18}.2H_2O$), with minor vaterite and/or aragonite scawtite. Immediately beneath the carbonated rim there is often a narrow region of enhanced porosity. Within this zone, carbonation of the CSH resulted in shrinkage and microfissuring of the carbonated CSH. The CSH in the walls of the microfractures is altered and leached of Ca to produce a residual microporous silica-rich gel-like alteration product. The fractures may become filled with fine grained calcium carbonate to form fine veins. These veins may be banded suggesting that shrinkage and dilation of fractures, followed by calcite precipitation, occurred in multiple cycles.

The late-stage carbonation and alteration of hydrated larnite nodules are clearly the result of low temperature alteration processes because they replace phases like tobermorite and CSH gels that must have formed through low-temperature interaction between groundwater with larnite. However, it is unclear whether the carbonation results from interaction between CSH phases and atmospheric CO_2 during exposure and weathering, or whether the carbonation results from the interaction with groundwater bicarbonate when the rocks were below the water table (i.e. before uplift). The presence of euhedral secondary calcite crystals lining the surfaces of fractures within the carbonation zones altered larnite-CSH nodules suggests that the calcite crystals grew in water-saturated pores. Meniscus cements more typical of precipitation under unsaturated conditions were not observed. Further research is required to more definitively ascertain the origin of the CO_2 and to determine whether carbonation is still ongoing.

1 Introduction

1.1 GENERAL

It is now widely accepted the rising levels of carbon dioxide (CO_2) in the Earth's atmosphere are causing global climate change, and this is a subject of international concern (e.g. IPCC, 1990, 2007). Furthermore, if something is not done to reduce emissions of greenhouse gases to the atmosphere, predictions suggest an unprecedented rate of future temperature increase, with unknown, but possibly rapid, consequences for the global climate. In order to stabilise atmospheric CO_2 concentrations at current values, it may be necessary to reduce CO_2 emissions by 60% or more over the next 50 years (RCEP, 2000). Assuming that we continue to burn fossil fuels, yet wish to mitigate CO_2 emissions to the atmosphere, we are faced with a limited number of alternatives, one of which is to dispose of the CO_2 in another domain of the planet, such as the geosphere (e.g. IPCC, 2005). By storing vast volumes of CO_2 securely without any land use or verification problems, we may be able to redress some of the imbalance between producing CO_2 and wanting to limit emissions to the atmosphere. One possible location for such a store is within porous rocks underground (the geosphere). In essence, geological storage aims to put the carbon directly back into the place from which it originally came (in the form of fossil fuels), thereby avoiding the atmospheric part of the carbon cycle.

A crucial aspect of geological storage is that the natural and man-made seals holding the CO_2 underground will remain effective for a considerable time. However, the operational design life of a typical oil well does not usually exceed 25-30 years, but efficient sealing of boreholes used in CO_2 storage operations requires a considerably longer lifetime, measurable in hundreds or thousands of years. It is very important therefore to understand the behaviour of borehole materials in the longer term, as the engineered seals around boreholes may provide routes for CO_2 migration *regardless* of how effective the caprock seal is.

In order to increase our understanding of the behaviour of borehole infrastructure in the presence of CO_2, a specific research activity (JRAP-14) was initiated within the CO_2GeoNet project (an EC-funded project, and part of the 6th Framework Programme). The programme of work undertaken within JRAP 14 included researchers from the British Geological Survey (BGS), Institut Français du Pétrole (IFP), Imperial College of London (ICL) and the Bureau de Recherche Géologique et Minière (BRGM). The overall aims of this research activity are to understand the reactivity and impact of CO_2 on borehole materials (especially borehole cement), how these change over time, and to assess the effects of these on borehole sealing. This has involved, literature reviews (see Rochelle et al., 2008), laboratory experiments lasting several months (Rochelle et al., 2009), predictive computer modelling (Rochelle et al., 2009), and studies of natural analogues to assess long-term processes (the subject of this report).

This report describes the results of a study of the alteration of naturally-occurring calcium silicate and calcium silicate hydrate (CSH) phases from Scawt Hill and Carneal Plug in Northern Ireland, United Kingdom. At these sites CSH phases will have interacted with atmospheric or soil CO_2, or with dissolved HCO_3^- in groundwater, providing a "natural analogue" for the potential long-term reactivity, stability and alteration behaviour of important CSH phases in borehole cements. Information obtained from this study may help to constrain predictive computer modelling of borehole systems, and provide an insight into the potential long-term alteration of cement as a result of carbonation reactions.

1.2 NATURAL ANALOGUES OF CEMENT

Natural analogues in which either the groundwater chemistry or mineral systems are similar to those encountered in man-made Portland cement systems are very rare, and are known from only a small number of restricted geological environments (Milodowski et al., 1989; Rochelle et al., 2008). Four principal occurrences of cement natural analogue systems can be defined:

1. Low-temperature serpentinisation of ultrabasic rocks and ophiolites, examples of which include Ophiolite complexes in Oman, Cyprus, Bosnia, California, Philippines, Japan and New Caledonia (Neal and Stanger, 1984; Stanger and Neal, 1984; Alexander et al., 2008a,b; Alexander and Milodowski, 2009 (in press); Anraku et al., 2009 (in press)). In this environment, hyperalkaline $Ca(OH)_2$ (±Na, K)-type groundwaters analogous to cement porewaters are produced by the alteration of calcic plagioclase and other calcium rich silicates. Precipitates formed from these groundwaters include CSH minerals such as portlandite, suolinite and tobermorite, which are analogous to phases found in hydrated Portland cement.
2. Retrograde alteration and hydration of metamorphic calcium silicates of high temperature-low pressure contact metamorphic zones around igneous intrusions in impure limestones and calcareous shales (Tilley, 1929, 1930, 1933; Tilley and Alderman, 1934; Tilley and Harwood, 1931; Tilley and Vincent, 1948; McConnell, J.D.C., 1954; 1955; Burnham, 1959; Milodowski et al., 1989; Grapes, 2006). The retrograde hydration of high-temperature contact-metamorphic minerals, similar to those found in cement clinkers (e.g. larnite, bredigite, spurrite, paraspurrite, scawtite), produces a low-temperature alteration assemblage of crystalline and non-crystalline CSH minerals analogous to phases found in hydrated cement paste.
3. Retrograde alteration and hydration of small bodies of high temperature – low pressure marble produced by spontaneous combustion and in-situ calcination (pyrometamorphism) of organic-rich argillaceous and siliceous limestones (e.g. Bender, 1968; Bentor et al., 1963a,b, 1972; Kolodny, 1970; Bentor and Kastener, 1976; Gross, 1977; Khoury and Nassir, 1982; Sabine, 1975; Sabine et al., 1982, 1985; Milodowski et al., 2001; Alexander, 1992; Linklater, 1998; Smellie, 1998, 2001; Glasser, 2001; Grapes, 2006)
4. Alteration of high temperature – low pressure metamorphic minerals produced by pyrometamorphism of coal seams and other carbonaceous sediments (Grapes, 2006). Examples of this can be found in Butte, Montana, coal seam fires of Pliocene-Holocene age in northwest China, the Injana area of Iraq, British Columbia, and in the Cretaceous "Smoking Hills" area in Franklin Bay in the Arctic Inuvik Province of Canada (Grapes, 2006).

In all of these geological systems, natural analogue cement minerals may potentially be altered as a result of carbonation through direct contact with atmospheric or soil gas CO_2, or by interaction with rainwater containing dissolved CO_2, or bicarbonate-type groundwaters.

The most detailed study of natural analogues of cement has been carried out at the Maqarin site (Yarmouk Valley) in northern Jordan. This site has been the subject of several detailed international research programmes funded by the European, Canadian and Japanese radioactive waste management industry and regulatory bodies, as an analogue for the long-term behaviour and evolution of the cementitious engineered barrier system of a geological repository for radioactive wastes (Alexander, 1992; Linklater, 1998; Smellie, 1998; Milodowski et al., 2001). At Maqarin, natural in-situ combustion of fractured, Upper Cretaceous-Lower Tertiary (Bituminous Limestone Formation) organic-rich, clay biomicrite limestone (bituminous 'marls') and siliceous chalks has calcined the sedimentary carbonate formations and produced discontinuous 'lenses' of high-temperature, low-pressure pyrometamorphic rocks (larnite-spurrite-paraspurrite-wollastonite-brownmillerite marbles belonging to the sanidinite and

pyroxenite hornfels metamorphic facies) (Khoury and Nassir, 1985; Alexander, 1992; Clark et al., 1993; Linklater, 1998; Smellie, 1998; Milodowski et al., 2001; Pitty, in press). Combustion-metamorphism occurred when the strata were unsaturated, and geomorphological and limited radiometric dating evidence places the metamorphic event between 150,000 and 600,000 years BP (Linklater, 1998; Smellie, 1998). The resultant metamorphic zone comprises marbles with a primary calcium silicate- and calcium aluminate-calcium-ferrite-rich mineral assemblage analogous to that found in Portland cement clinker. Subsequently, a progressive regional rise in the groundwater level resulted in low temperature hydration and re-carbonation of rock in these metamorphic zones. This produced (and the process is still ongoing within an active groundwater system) a complex assemblage of hydration and alteration products equivalent to those found in hydrated Portland cement (including; portlandite, brucite, tobermorite, jennite, poorly-crystalline CSH gels, calcite, opal-CT and opal-A (Alexander, 1992; Linklater, 1998; Smellie, 1998; Milodowski et al., 2001; Pitty in press). Portlandite is present as a major rock-forming mineral in these re-hydrated rocks. Groundwaters circulating through this 'cement zone' (the metamorphic rocks and their hydrated equivalents) are buffered between pH 12.5 and pH 13 by reaction with portlandite and CSH minerals Several similar pyrometamorphic zones are found within similar rocks in the equivalent stratigraphical horizons in central Jordan (Daba Marble) and Israel (Hatrurim Formation) but there are no longer any active hyperalkaline groundwater systems at these 'fossil' sites.

The pyrometamorphic rocks from Maqarin, central Jordan and Israel and their retrograde alteration products represent the best possible natural analogues of a hydrated Portland-type cement system. They represent examples of naturally-calcined rocks that are very 'broadly similar' to the raw materials used in Portland cement manufacture (i.e. basically a mixture clay and limestone), and their subsequent hydration. Archive materials from the radioactive waste analogue studies at Maqarin and central Jordan (op. cit.) are held by the BGS. However, the samples were collected primarily to study: the geochemical behaviour of trace elements analogous to waste radionuclide species, and; the interactions of the alkaline groundwaters emanating from the hydrating pyrometamorphic rocks with the surrounding country rocks as an analogue for alkaline plume from a cementitious repository with the surrounding geosphere. Unfortunately, very little of the archived sample material is suitable for studying carbonation reactions associated with the interaction between background bicarbonate-type regional groundwaters and the hydrated pyrometamorphic rocks. Further sampling of these sites was outside the scope of the present study because of budget constraints and security issues related to the unstable political situation in the Middle East at the time.

The work reported here focussed on a study of the carbonation reaction behaviour of naturally-occurring cement mineral assemblages associated with the high-temperature low-pressure contact metamorphic aureoles around minor Tertiary dolerite intrusions into Cretaceous siliceous limestones (Chalk) in Northern Ireland. These sites were examined in a previous natural analogue study of the hydration and long-term evolution of calcium silicate hydrate (CSH) phases (Milodowski et al., 1989). This study also identified alteration related to late-stage carbonation of the CSH phases, which suggested these sites might furnish potentially useful natural analogue information on the effects of interaction between cement and CO_2.

2 Site descriptions, geology and sample locations

The Antrim Lava Group (Palaeogene) of Northern Ireland is intruded by at least thirty dolerite plugs that in places form prominent landmarks rising above the surface of the Antrim Plateau (Mitchell, 2004). These minor intrusions are roughly circular in outline or elongated in a NNW-SSE direction that is parallel to the orientation of the main dyke swarm. They vary from 50 m to 1 km in diameter and are composed mainly of olivine dolerite. Many of the plugs are associated with contact metamorphism of the adjacent country rocks. Four of these plugs – Scawt Hill, Carneal, Ballycraigy and Ballygalley - have intruded chert (flint)-bearing Upper Cretaceous Ulster White Limestone Formation (Chalk). At Scawt Hill, Carneal Plug and Ballycraigy Plug limestone and chert nodules have been hornfelsed by the dolerite producing a calcsilicate mineral assemblage (Tilley, 1929, 1930. 1933, Tilley and Alderman, 1934; Tilley and Harwood, 1931, Tilley and Vincent, 1948, Sabine, 1975, Sabine et al., 1982, 1985; Griffith and Wilson, 1982; Mitchell, 2004). Although much larger than Carneal and Ballycraigy, surprisingly no contact metamorphism has been reported from the Ballygalley Plug (Griffith and Wilson, 1982; Mitchell, 2004).

A short field visit to Northern Ireland was undertaken in July 2007 to examine and collect samples of the calcsilicate hornfels rocks and their alteration products from Scawt Hill, Carneal, Ballycraigy and Ballygalley.

2.1 SCAWT HILL

Scawt Hill (National Grid Reference D3380 0900) is located about 5 km west-northwest of Ballygalley and 7 km south-southeast of Glenarm, County Antrim. The hill is a very conspicuous feature, at the edge of the east-facing Antrim basalt escarpment, rising some 30 m above the surrounding flat Tertiary flood-basalt plateau, to a height of 378 m O.D (Plate 1).

Plate 1. View of Scawt Hill, looking north from near Ballycraigy, County Antrim, Northern Ireland. The hill rises as a prominent knoll above the flat Antrim Plateau Escarpment (Tertiary Lower Basalt Formation).

Scawt Hill is formed by a moderately large olivine-dolerite plug of Palaeogene age that intrudes both the Cretaceous Ulster White Limestone Formation and early Palaeogene lavas of the Lower Basalt Formation (Geological Survey of Northern Ireland, 2001, Mitchell, 2004) (Figure 1). The curved well-jointed cliff that forms the southeast face of the hill (Figure 2 and Plate 2) follows the plug margin. The actual contact between the Ulster White Limestone Formation is exposed in steep gullies at the southeast and northwest of the hill (Figure 2). The contact is best exposed at the southeastern end of the hill, where the cliffs expose a thin veneer of metamorphosed Ulster White Limestone Formation (marble) adheres to the vertical walls of the dolerite plug (Plate 3).

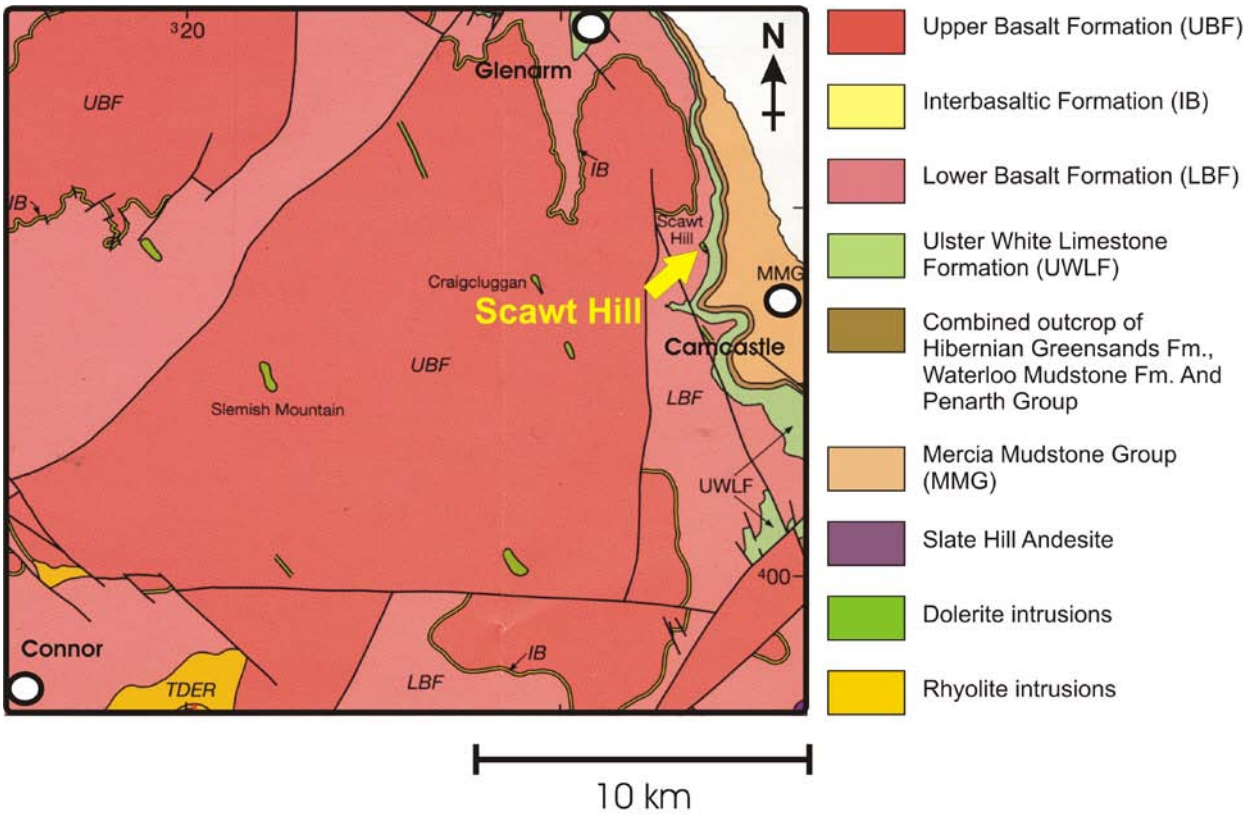

Figure 1. Simplified map of the solid geology of the Scawt Hill area, showing the location of the Scawt Hill dolerite plug intruding the Ulster White Limestone Formation at the eastern edge of the Antrim Plateau basalt escarpment (taken from Geological Survey of Northern Ireland, 2001, © Crown Copyright 2001)

A large landslipped block of marble and weakly metamorphosed Ulster White Limestone Formation also emerges through an apron of scree at the foot of the centre of the southeast face of the hill (Figure 2, Plate 2 and Plate 4). However, the contact between the dolerite and the limestone is not seen in this area of the hill. Abundant fallen blocks of unmetamorphosed Ulster White Limestone Formation containing chert concretions and marble with calcsilicate nodules (representing hornfelsed chert) are found in the scree at the foot of the this slope. When freshly broken open, many of the fallen blocks of marble were found to contain highly altered calcsilicate (larnite) nodules that were virtually completely replaced by a very moist, soft white gel-like alteration product (Plate 5). On exposure to air this material rapidly lost water and dried to hard creamy-white gel with shrinkage cracks. These highly hydrated altered calcsilicate nodules were dissolved away to leave mouldic cavities on weathered rock surfaces.

Samples of marble, containing altered and unaltered calcsilicate nodules, were collected for detailed mineralogical and petrographical analysis from the contact zone at the southeast of the hill and from the fallen blocks of scree in the area at the foot of the landslipped limestone block.

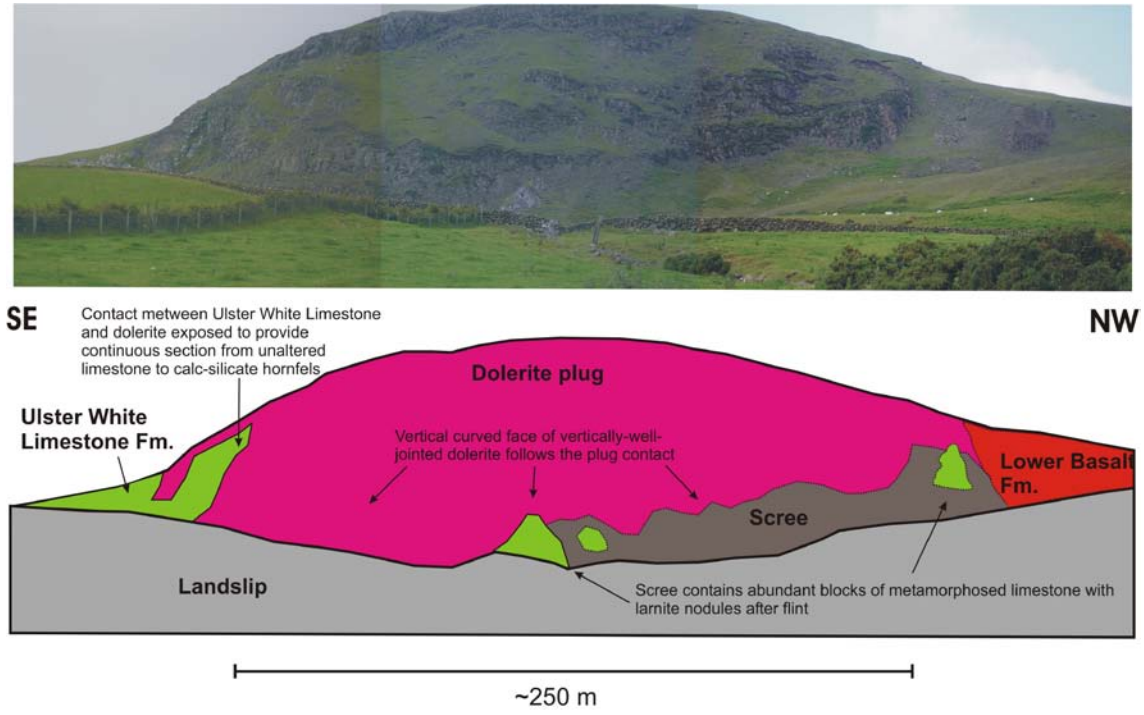

Figure 2. Photograph of the southeast face of Scawt Hill (top) and simplified sketch of the main geological features of the exposed dolerite plug and the adjacent country rocks (bottom).

Plate 2. View to the northwest along the subvertical dolerite joint surfaces that form the southeast face of Scawt Hill. This face represents the original margin of the plug. A large landslipped block of Ulster White Limestone Formation (centre) emerges out of grass-covered scree at the foot of this cliff face.

Plate 3. Southeastern end of Scawt Hill showing the contact between the Ulster White Limestone Formation and the dolerite plug. The contact metamorphosed limestone forms a thin veneer adhering to the vertical walls of the dolerite plug.

Plate 4. Closer view of the centre of the southeast face of Scawt Hill. It shows a large landslipped block of metamorphosed Ulster White Limestone (centre), surrounded by an apron of grass-covered scree, situated in front of the subvertical darker brown dolerite cliff face that represents the margin of the plug.

Plate 5. Very hydrous gel-like phase formed by hydration and alteration of a calcsilicate (larnite) nodule, which was revealed in a freshly broken open block of marble from Scawt Hill.

The petrology and mineralogy of the contact metamorphic calcsilicate rocks from Scawt Hill have been described in detail by Tilley (1929, 1930. 1933), Tilley and Alderman (1934), Tilley and Harwood (1931), Tilley and Vincent (1948) and are briefly summarised by Mitchell (2004). In general the metamorphosed cherts display progressive marginal metasomatism with larnite-spurrite-dominated rock formed at the margins of the former chert (adjacent to the limestone matrix) surrounding a core of wollastonite and xonotlite. However, they may contain a complex assemblage of other primary metamorphic minerals including quartz, scawtite, bredigite, melilite, spinel, gehlenite, merwinite, magnetite. Later retrograde hydration and meteoric alteration have resulted in the formation of a range of secondary CSH minerals including xonotlite, tobermorite, afwillite, gyrolite and ettringite.

Large landslips affect much of the area underlain by Mesozoic sedimentary strata (Figure 1) to the east of the basalt escarpment. At Scawt Hill landslipped strata form the undulating lower lying pasture land beneath extending to the southeast from foot of the steep dolerite cliffs (Figure 2). These major landslips are most likely to have occurred along the steep margins of the Antrim Plateau shortly after the retreat of ice cover at the end of the last glacial maximum (24,000 to 20,000 years BP), when the ice support was lost (Mitchell, 2004).

2.2 CARNEAL PLUG

The Carneal Plug (National Grid Reference X3390 3959) is located to the south of Larne, at the junction of the Carneal and Raloo Waters, about 0.8 km southwest of the village of Glenoe. It is a small Tertiary dolerite plug intruded through the Lower Basalt Formation (Griffith and Wilson, 1982; Mitchell, 2004). The plug is roughly circular in diameter and approximately 100-120 m in diameter (Figure 3), and it lies immediately to the west of the NNW-trending Carneal Fault, a normal fault which is downthrown to the east. It forms a small flat-topped knoll beside the flood plain of the two streams. The eastern margin of the plug is sheared, and this shearing also affects a large xenolith of Ulster White Limestone Formation.

The plug comprises a central core of coarse grained ophitic olive dolerite, with a outer marginal zone of pyroxenite containing large xenolithic inclusions of fine-grained, hornfelsed, hard white

limestone (bedded with flints) up to 10 m across (Griffith and Wilson, 1982). Finer grained basaltic grain sized rock may be seen in the margin in the northwest corner of the intrusion and represents chilling. The limestone xenoliths have been dragged up by the intrusion from the Ulster White Limestone Formation that underlies the Lower Basalt Formation in this area (Emelius and Preston, 1969; Griffith and Wilson, 1982; Mitchell, 2004). The Ulster White Limestone Formation is seen at outcrop 1 km south of the plug, near Carneal Bridge but the depth at which it underlies the area of the plug is unknown, though it is believed to of the order of a few tens of metres (Griffith and Wilson, 1982).

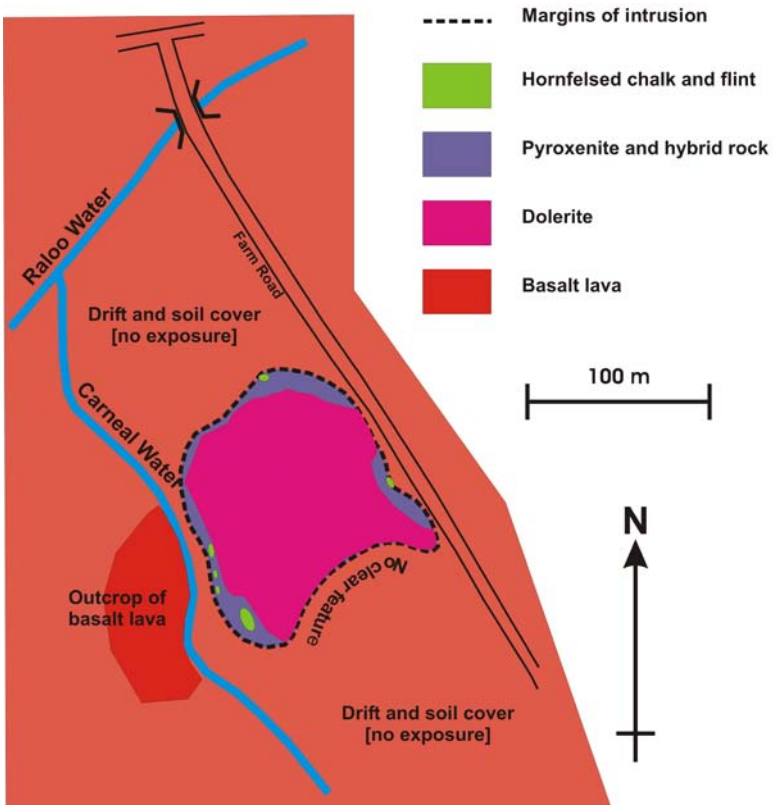

Figure 3. Geological map of Carneal Plug showing location of hornfelsed xenoliths of chalk (Ulster White Limestone Formation) and flint included within the hybridised (pyroxenitic) margins of the dolerite intrusion (based on Griffith and Wilson, 1982).

The petrology of the Carneal Plug and its associated metamorphosed limestone xenoliths are described in detail by Sabine (1975), Sabine et al. (1982, 1985) and summarised by Griffith and Wilson (1982). Partial assimilation of the limestone by the dolerite magma has locally produced the hybrid black pyroxenite and mixed pyroxenite-larnite rocks forming the outer margin of the plug (Figure 3). The xenolithic inclusions of Ulster White Limestone are best exposed on the western side of the plug, where it was once worked in a small quarry that is now disused and heavily overgrown in gorse and woodland (Plate 6). These xenoliths have been intensely thermally metamorphosed, metasomatised to form a calcsilicate-rich marble, although the outlines of original chert (flint) concretions are still recognisable in the larger xenoliths. However the original calcite and silica have been completely altered and replaced by calcsilicate rock containing a complex assemblage of minerals that includes: quartz, larnite, wollastonite, spurrite, bredigite, merwinite, gehlenite, calcite, spinel, scawtite, perovskite, hibschite (hydrogrossular), titanite (sphene) and magnetite, together with their low-temperature alteration products such as xonotlite and tobermorite (Sabine, 1975, Sabine et al., 1982, 1985). The former chert nodules commonly exhibit dark reaction rims. P-T measurements based on mineral phase relationships (Sabine, 1975; Sabine et al., 1982, 1985; Grapes, 2006) indicate metamorphism

occurred at very high temperatures (probably between 1050-1100 °C) and low pressure (c.200 bars).

Plate 6. Metasomatised and partially assimilated xenolith of Ulster White Limestone Formation exposed in an overgrown and degraded old quarry face on the east side of Carneal Plug.

Plate 7. Highly metasomatised and partially assimilated hornfelsed xenolith of Ulster White Limestone Formation rock, containing metamorphosed chert concretions. The rock is irregularly veined by dark hybrid pyroxenite. Carneal Plug.

Several samples of metamorphosed and metasomatised chert nodules were collected from limestone xenoliths exposed in the highly degraded small quarry faces exposed on the western side of the plug (Plate 6 and Plate 7).

2.3 BALLYCRAIGY PLUG

Ballycraigy Plug (National Grid Reference D 3870 0450) is located between Brustin Braes road and Killyglen Burn, about 2 km north of Larne and 3.5 km southeast of Carncastle. The plug is a nearly circular intrusion about 150 m average diameter. The site originally exposed crags of very coarse-grained dark grey olivine-dolerite surrounded by Cretaceous Greensand and Chalk, which were intruded and metamorphosed by the dolerite. The dolerite was reported to be locally gabbroic in texture, in places with large vesicles carrying larnite with tobermorite as a fibrous lining to vugs, and a poorly crystalline CSH gel (plombierite) formed as a hydration product of both larnite and bredigite (McConnell, 1954).

Unfortunately, much of the site was found to be now densely overgrown or covered in rough pastureland, with very little exposure remaining. Neither contact metamorphic rocks nor vesicular gabbroic dolerite are now exposed. Consequently, no suitable samples of natural analogue material could be obtained for study from this site.

2.4 BALLYGALLEY HEAD

Ballygalley Head (National Grid Reference D 3830 0770) is a large dolerite plug that forms a rocky coastal headland 8 km north of Larne (Plate 8). It is intruded into the Ulster White Limestone Formation. Emelius and Preston (1969) suggest that is has chalky agglomerates and exhibits a good contact with the Ulster White Limestone Formation exposed in the quarry adjacent to the coastal road. However, it has also been noted that although the dolerite intrusion is much larger than the Ballycraigy Plug there appeared to be very little metamorphic alteration of the Ulster White Limestone Formation which it intrudes (Griffith and Wilson, 1982; Mitchell, 2004).

Plate 8. View southeast from Scawt Hill to Ballygalley Head, which forms the prominent rocky headland in the distance.

The quarry referred to by Emelius and Preston (1969) is now disused and heavily overgrown, and the contact between the Ulster White Limestone Formation and the dolerite is no longer visible. Elsewhere, the contact between the dolerite and the Cretaceous country rocks is also obscured, and it is possible that it is partially covered by recent landslip (indeed a significant landslip occurred cutting the coastal road just to the south of this site at the time of the field

visit). No metamorphic calcsilicate rocks could therefore be observed or sampled for analysis at this site.

2.5 SAMPLES

A total of 15 samples of altered calcsilicate hornfels rock were collected from the metamorphic contacts at Scawt Hill and Carneal Plug. A summary of background samples information is presented in Table 1.

Table 1. Summary information for samples of cement natural analogue material from Northern Ireland.

Site	Laboratory Sample Code	Field Sample Code	Sample description
Carneal Plug	MPLM789	CP_01_07a	Multiple samples of altered hornfelsed chert larnite nodules with CSH hydration products
	MPLM790	CP_01_07b	Near to the contact: dolerite, chert and marble/chalk
	MPLM791	CP_01_07c	Cavities after altered larnite nodules (hornfelsed flints) enclosed by closely crystalline grey marble matrix, with in-situ altered CSH gel and residual larnite nodule surrounded by microporous alteration rim
	MPLM792	CP_01_07d	Near to the contact: fragments of dolerite, chert and marble/chalk
	MPLM793	CP_01_07e	Weathered fallen block containing dissolution cavities after eroded hornfelsed cherts.
	MPLM794	SC_01_07	Altered and hydrated hornfelsed cherts
Scawt Hill	MPLM795	SC_Scree_Slope	Multiple samples and fragments of white or cream coloured altered and hydrated larnite nodules (hornfelsed cherts) in grey coarsely crystalline marble. Heavily fractured
	MPLM796	SC_01_07	Freshly exposed large hydrated larnite nodule, with very soft gel-like CSH alteration product
	MPLM797	SC_02_07	Altered and hydrated larnite nodules with concentric banding
	MPLM798	SC_03_07	Large altered and weathered larnite nodule (hornfelsed flint)
	MPLM799	SC_04_07	Cavity in marble, after weathering out of larnite nodule in situ on rock face, preserving a carbonated hydrated larnite reaction rim.
	MPLM800	SC_05_07	Soft gel-like alteration material formed by hydration of larnite nodule
	MPLM801	SC_06_07	Hydrated larnite nodules with alteration rim
	MPLM802	SC_07_07	Hydrated larnite nodules with alteration rim
	MPLM803	SC_08_07	Hornfelsed chert, in medium grained marble. Pale, soft CSH formed as a reaction rim. Taken from the margin of the intruded dolerite

3 Analytical methodology

3.1 GENERAL

The altered calcsilicate hornfels samples were initially sawn in two to produce a flat fresh surface that exposed a profile through each nodule. These cut surfaces were then photographed with a digital camera before taking subsamples for mineralogical and petrographical analyses.

The bulk mineralogical composition of the nodules was determined by X-ray diffraction (XRD) analysis. Where discrete alteration banding or zoning could be seen in the cut surfaces, each distinct band was subsampled for XRD analysis to provide information on the mineralogy of that specific band. Subsamples of the discrete bands were carefully taken from the cut surface using a small hand-held diamond saw mini-tool, and or prised away with a small chisel.

Polished thin sections were prepared from the nodules for petrographical analysis. The sections were cut to sample a profile from the outer edge of the nodule to the centre of the nodule. Some larger nodules required more than one section in order to examine the nodule from the centre to the rim. Polished sections were prepared by cutting thin slices of the nodule and impregnating them with epoxy-resin under vacuum in order to stabilise the material for polished section preparation. These resin-impregnated blocks were then cut and polished under ethanol (to prevent reaction of water-sensitive cement phases with standard water-based cutting fluids) to produce polished thin sections 30 µm thick bonded onto 45 x 28 mm glass microscope slides with a colourless epoxy-resin. A blue dye was added to the epoxy-resin prior to vacuum impregnation to differentiate between porosity originally present within the vacuum-dried sample and artefacts of the sectioning process (e.g. grain plucking), when the sections were observed by transmitted-light microscopy. The sections were finished to a high-quality polish with 0.45 µm diamond paste.

Prior to detailed petrographical observations by backscattered scanning electron microscopy, the polished thin sections were briefly examined in transmitted light using a Zeiss Axioplan 2 optical petrographical (polarising) microscope.

3.2 X-RAY DIFFRACTION ANALYSIS

3.2.1 Sample preparation

For quantitative whole-rock XRD analysis, the samples were ground in pestle and mortar and a c.3 g portion of the ground material was then wet-micronised under acetone for 10 minutes, dried, disaggregated and back-loaded into standard stainless steel sample holders for analysis.

Where insufficient material was available to prepare a standard back-loaded sample mount, a portion of the ground material was deposited onto the surface of a ‘zero-background’ silicon crystal wafer mount using a single drop of acetone.

3.2.2 Analysis

XRD analysis was carried out using a PANalytical X’Pert Pro series diffractometer equipped with a cobalt-target tube, X’Celerator detector and operated at 45kV and 40mA. The samples were scanned from 4.5-85°2θ at 2.76°2θ/minute. Diffraction data were initially analysed using PANalytical X’Pert Highscore Plus Version 2.2a software coupled to the latest version of the International Centre for Diffraction Data (ICDD) database.

Following identification of the mineral species present in the samples, mineral quantification was achieved using the Rietveld refinement technique (e.g. Snyder and Bish, 1989) using PANalytical Highscore Plus software. This method avoids the need to produce synthetic mixtures and involves the least squares fitting of measured to calculated XRD profiles using a crystal structure databank. Errors for the quoted mineral concentrations are typically ±2.5% for concentrations >60 wt%, ±5% for concentrations between 60 and 30 wt%, ±10% for concentrations between 30 and 10 wt%, ±20% for concentrations between 10 and 3 wt% and ±40% for concentrations <3 wt% (Hillier et al., 2001). Where a phase was detected but its concentration was indicated to be below 0.5%, it is assigned a value of <0.5%, since the error associated with quantification at such low levels becomes too large.

3.3 BACKSCATTERED SCANNING ELECTRON MICROSCOPY

Backscattered scanning electron microscopy (BSEM) analyses were carried out using a LEO 435VP variable pressure digital scanning electron microscope (SEM) fitted with a solid-state 4-element (diode) backscattered electron (BSEM) detector. The SEM instrument was also equipped with an Oxford Instruments INCA Energy 350 energy-dispersive X-ray microanalysis (EDXA) system with a thin window Si-Li X-ray detector capable of detecting elements from boron to uranium.

Polished thin sections were coated with a thin layer of carbon (approximately 250Å thick) before being examined in detail by BSEM. Samples were imaged by BSEM using a 10-20 kV electron beam accelerating potential, beam currents between 200-800 pA, and a working distance of 17-20 mm, as required.

The BSEM image brightness is proportional to the average atomic number of the material, thus allowing the differentiation of phases on the basis of their chemistry (Goldstein et al., 1981). Phase identification was also aided by microchemical information obtained from observation of semi-quantitative EDXA spectra recorded from features of interest.

4 Mineralogical observations

4.1 ALTERATION OF CALCSILICATE NODULES FROM CARNEAL PLUG

XRD analyses of the altered hornfelsed chert nodules are presented in Table 2. Macroscopically, the hornfelsed chert (calcsilicate) nodules still resemble the original chert concretions, retaining their original morphology. All the nodules display brecciation (probably related to volume changes during metamorphic alteration) and their metamorphic mineralogy and features are broadly similar in to those described previously by (Sabine, 1975, Sabine et al., 1982, 1985).

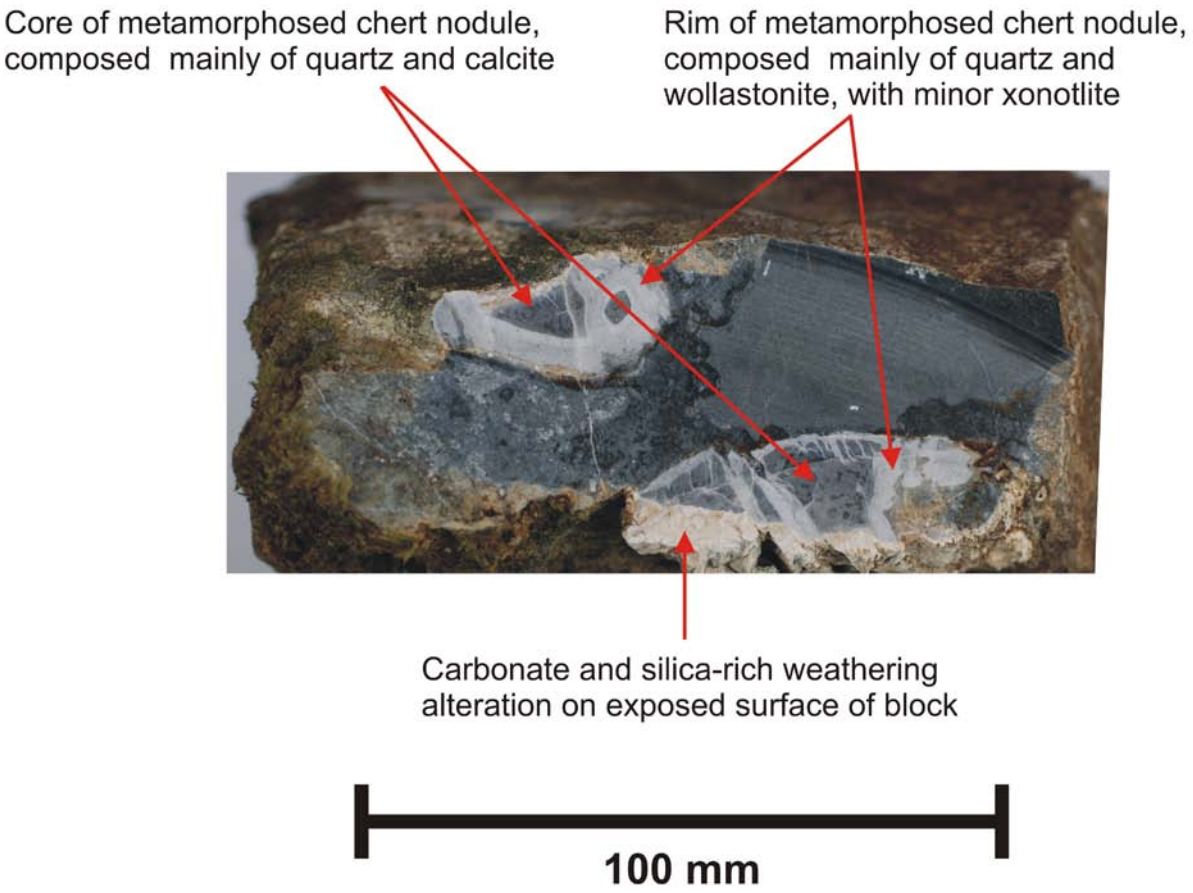

Plate 9. Section through an altered calcsilicate nodule (sample MPLM793) from Carneal Plug. It shows two brecciated nodules with grey cores composed largely of quartz with minor calcite (Zone 1), surrounded by a white reaction rim composed mainly of wollastonite and quartz, with minor xonotlite (Zone 2). The dark matrix between the former chert nodules is metasomatised larnite-pyroxene-magnetite-rich marble, with abundant secondary CSH hydration products formed around the margins of metamorphosed cherts (seen as colloform darker patches enclosed by unaltered lighter grey matrix material – Zone 3). A creamy-white late stage microporous carbonate and silica-rich alteration crust is seen on the outer exposed and weathered surfaces of the block (Zone 4)

The calcsilicate nodules usually contain a dark grey core of largely coarsely crystalline quartz, representing residual recystallised but unreacted original chalcedonic chert material (e.g. Plate 9; Zone 1) with minor to trace amounts of calcite sometimes present. The dark grey core is

surrounded by a white reaction rim comprising an intergrowth of coarsely crystalline major quartz and wollastonite, where the original chert nodule has reacted completely with Ca introduced into the chert during metamorphism (e.g. Plate 9; Zone 2). BSEM-EDXA observations suggest that this reaction zone may also contain a small amount of more calcic larnite in addition to wollastonite but this was not confirmed by XRD (Table 2). Traces of aragonite, gibbsite and anorthite were also detected by XRD but could not be distinguished petrographically. The enclosing dark grey rock matrix was found to comprises a very complex intergrowth of brownmillerite, pyroxene, titanite, larnite, quartz, magnetite and possible andraditic garnet and represents limestone metasomatised by the addition of Fe, Mg, Ti and Al from the dolerite (i.e. skarn rock). The quartz-wollastonite rock is largely unaffected by alteration associated with very late-stage hydration and carbonation reactions. Although, xonotlite identified by XRD as a minor phase within Zone 2 may possibly relate to hydration alteration that occurred during low-temperature retrograde metamorphism described previously by Sabine (1975).

In contrast, the enclosing dark grey skarn rock displays significant alteration (Plate 9), associated with the development of abundant microporosity along the margins of the calcsilicate nodules (Plate 10), with nanoporosity within the matrix of the altered layers. XRD analyses (Table 2) of these altered and leached porous nodule margins showed that they are composed of major calcite, with minor quartz, larnite, tobermorite, vaterite and scawtite. In addition, trace amounts of magnetite, ankerite and brownmillerite were identified to be present. Palygorskite and ettringite were also tentatively identified as part of the alteration assemblage. Petrographical observations show that the alteration is generally extremely fine grained (Plate 11) and it was impossible to differentiate the calcium silicate-carbonate mineral scawtite from finely admixed intergrowths of secondary silica, calcium carbonate and CSH, and ettringite and palygoskite identified by XRD could not be recognised in thin section by either optical microscopy or BSEM-EDXA

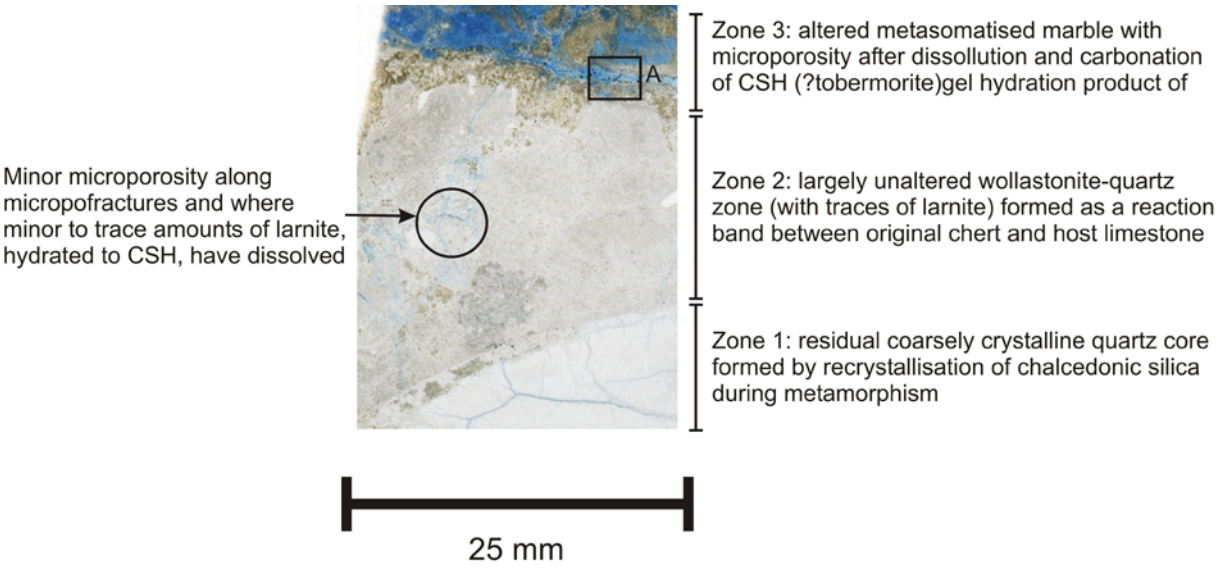

Plate 10. Transmitted light photograph of polished thin section through an altered calcsilicate nodule (sample MPLN789), Carneal Plug. Significant microporosity (revealed by blue-coloured epoxy-resin impregnation) is developed in larnite-rich marble matrix (Zone 3) at the margin of the nodule due to the carbonation and dissolution of secondary CSH gel formed by hydration of the larnite. Minor larnite dissolution within the wollastonite-quartz rock (Zone 2) has also produced fine microporosity. Further detail of area A is shown in Plate 11.

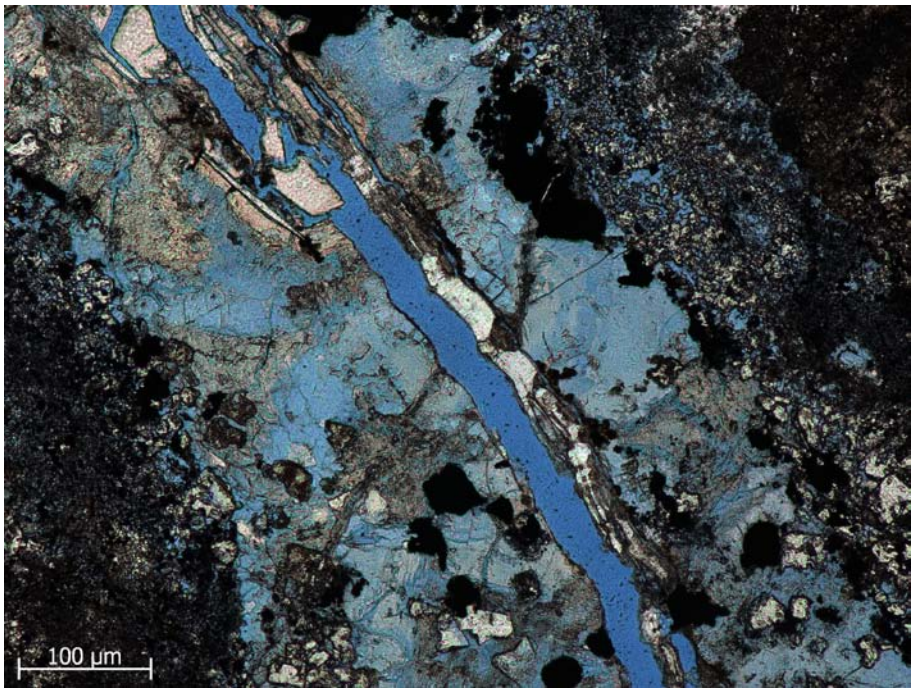

Plate 11. Transmitted light photomicrograph of alteration at the interface between granular wollastonite-quartz zone (bottom left) and larnite-bearing skarn host rock containing abundant opaque magnetite (top right). Microporous CSH gel (shown by blue epoxy-resin impregnation) is largely altered to Si-rich gel containing diffuse relicts of gel-like CSH with a higher Ca:Si ratio (seen as areas that are less intensely coloured by the blue epoxy-resin). The CSH alteration preserves the original grain outlines of the primary larnite. Microgranular calcium carbonate (uncoloured) has nucleated within the altered CSH gel and coarse calcite lines a microfracture created by shrinkage of the altered CSH gel. Area A in Plate 10, sample MPLN789, Carneal Plug.

Two stages of late-stage low temperature alteration can be differentiated:

1. The earliest alteration is the hydration and replacement of larnite by CSH gel. Optical petrography suggests that much of this CSH gel is isotropic (Plate 12) and therefore probably largely amorphous. However, XRD data (Table 2) shows that at least part of this CSH contains more crystalline 11Å tobermorite. Trace amounts of larnite intergrown within the underlying wollastonite-quartz reaction zone in the metamorphosed chert nodule may also be partially hydrated to amorphous or poorly crystalline CSH along networks of microfractures (Plate 10). The CSH alteration products preserve (pseudomorph) the original crystal grain boundaries of the primary larnite (Plate 11). This feature was observed in earlier studies of the hydration of larnite to CSH in calcsilicate nodules from Scawt Hill and Carneal Plug (Milodowski et al., 1989), and implies that the hydration of larnite to CSH/tobermorite is isovolumetric.
2. The second alteration stage involves the replacement of CSH by calcium carbonates. XRD suggests that the calcium carbonate mineral is dominantly calcite but minor to trace amounts of vaterite and aragonite are also formed. In addition, traces of ankerite were also identified. Vaterite has previously been recorded in association with CSH formed from by alteration of larnite nodules from Ballycraigy by McConnell (1960). The calcium carbonate has nucleated as patches or “islands” within the CSH gel matrix and along the fabric delineated by the original grain boundaries of the primary larnite. EDXA indicates that the residual CSH gel becomes increasing lower in Ca:Si as alteration progresses and the carbonate “islands” coalesce to form a microgranular groundmass. Eventually this alteration produces a fine grained mixture of calcium carbonate and probable silica gel. CSH replacement by calcium

carbonate is also accompanied by enhanced microporosity, as a result of volume reduction and polygonal shrinkage cracking of the CSH gel together with some dissolution of the gel matrix around the secondary carbonate (Plate 12). Porous microfractures are also produced along the interface between the wollastonite-quartz nodule and the host rock (Plate 11), often resulting in "popping-out" of the now only weakly-bonded nodule core. These fractures are commonly lined by secondary calcite mineralisation, the calcium presumably having been derived from Ca released during the alteration of the CSH substrate.

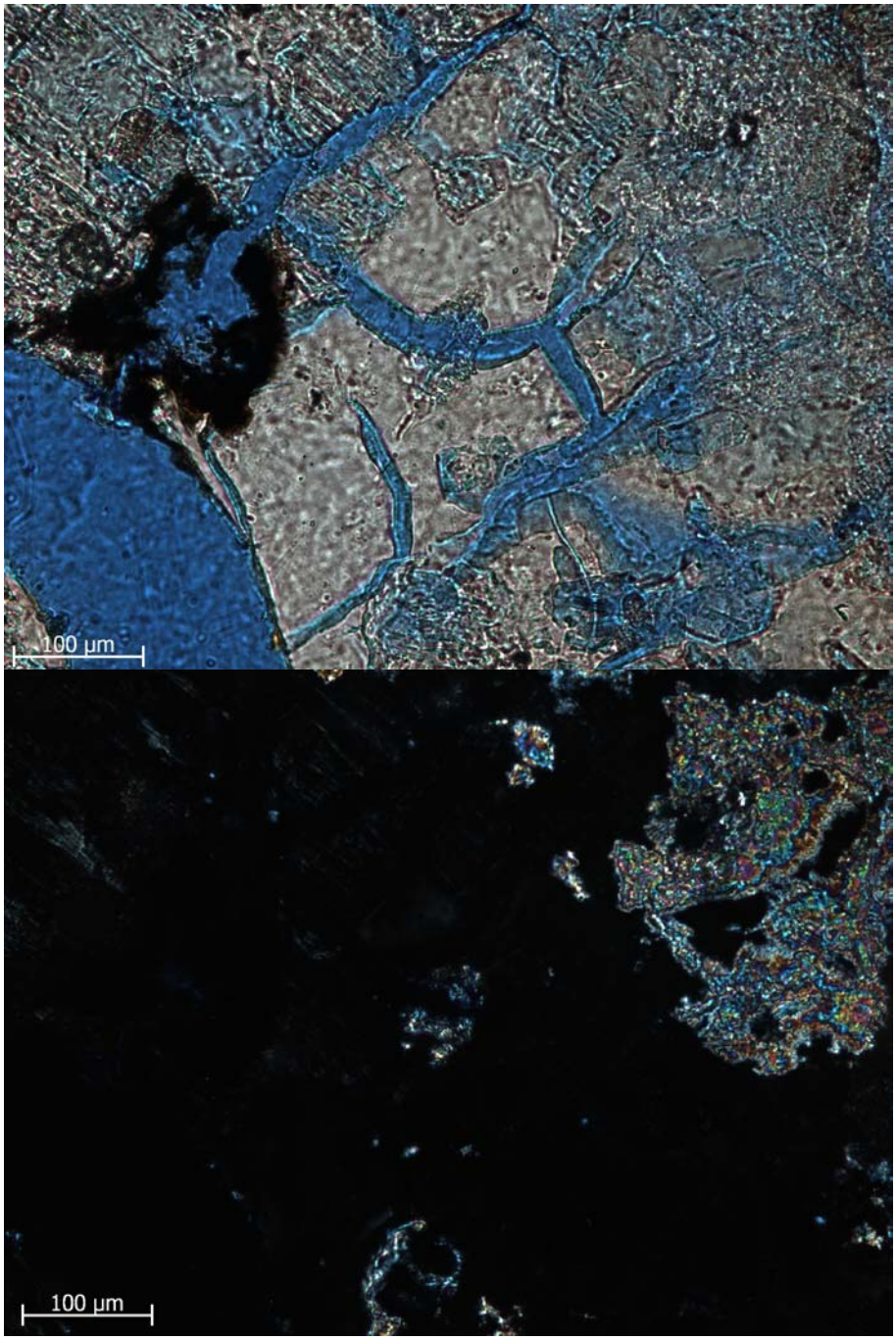

Plate 12. Top: Transmitted light photomicrograph (plane polarised light) showing detail of the shrinkage of CSH gel (clear) associated with its alteration and replacement by microgranular calcium carbonate and silica. Opaque grain is secondary goethite after primary magnetite. Bottom: same area under crossed polarised light showing isotropic nature of the CSH gel (black) and highly birefringent fine grained calcium carbonate replacing the CSH gel.

Table 2. Summary mineralogy of natural analogue cement samples from XRD analysis

Site	Laboratory Sample Code	Preparation method	Brief sample description	Mineral identification			Quantitative mineralogy																					Comments
				Major	Minor	Trace	ankerite	aragonite	brownmillerite	calcite	ettringite	gibbsite	gypsum	hydroxylapatite	larnite	magnetite	mica'	palygorskite	quartz	scawtite	smectite	spurrite	tobermorite-11A	tobermorite-14A	vaterite	wollastonite	xonotlite	
Carneal Plug	MPLM789	AB	outer reaction rim (c.1cm); grey-white	calcite	quartz, tobermorite-11A, vaterite, scawtite, larnite	magnetite, ?ettringite, ?palygorskite, ankerite, brownmillerite	0.5		<0.5	57.8	1.3				3.5	1.3		1.7	10.6	6.7			7.8		8.6			
	MPLM793-1	SW	grey inner core	quartz	calcite	aragonite, gibbsite		3.5		5.8		0.6							90.1									
	MPLM793-2	AB	white reaction rim	quartz, wollastonite	calcite, xonotlite	smectite				1.8									26.8		1.0					64.3	6.1	
	MPLM794	AB	whole-rock sample	quartz		calcite, ?anorthite				0.8									99.2									
Scawt Hill	MPLM796-1	SW	grey outer rim	calcite		quartz, scawtite				92.5									1.4	6.1								
	MPLM796-2	SW	white thin middle layer	calcite	gypsum	quartz, 'mica', ?scawtite				78.3			16.2				1.7		3.8									difficulty to identify minerals caused by broad and weak reflections
	MPLM796-3	AB	grey inner zone	paraspurrite, spurrite, calcite	larnite	scawtite																						no quantification possible as no icsd pattern for paraspurrite available
	MPLM799-1	SW	brown outer weathered rim	calcite	hydroxylapatite, quartz	brownmillerite			0.6	88.3				8.2					2.9									
	MPLM799-2	AB	white weathered inner zone	calcite	hydroxylapatite, quartz	mica', brownmillerite			<0.5	92.2				4.5			1.6		1.5									
	MPLM802b-1	AB	grey inner zone	calcite, paraspurrite	scawtite, spurrite	?wollastonite																						no quantification possible as no icsd pattern for paraspurrite available
	MPLM802b-2	SW	white very thin middle layer	calcite	scawtite	quartz, brownmillerite			<0.5	77.2									2.8	20								
	MPLM802b-3	AB	light grey outside rim	calcite, scawtite	quartz, tobermorite-14A	?palygorskite				62.7								1.1	1.2	31.8				3.2				
	MPLM802c	AB	whole-rock sample	quartz	calcite	wollastonite, gibbsite, spurrite				4.8		0.6							92.9			0.7				1		
	MPLM803	AB	white coating	calcite, smectite	quartz					66.7									3.5		29.8							stevensite-15A (saponite)

Notes		
	SW	Silicon wafer
	AB	whole-rock

Mineral name	Chemical formula
Brownmillerite	Ca2(Al,Fe)2O5
Ettringite	Ca6Al2 (SO4)3 (OH)12 ·26H2O
Hydroxylapatite	Ca10(PO4)6(OH)2
Larnite	Ca2(SiO4)
Palygorskite	(Mg,Al)2Si4O10(OH).4(H2O)
Scawtite	Ca7Si6(CO3)O18.2(H2O)
Paraspurrite	Ca5(SiO4)2(CO3)
Spurrite	Ca5(SiO4)2(CO3)
Tobermorite	Ca5 (OH)2Si6O16 ·4H2O
Vaterite	CaCO3
Wollastonite	CaSiO3
Xonotlite	Ca6Si6O17(OH)2

The late-stage carbonated alteration zone contains significant scawtite in addition to calcite, aragonite and vaterite. However, it is unclear whether the scawtite is part of the high-temperature retrograde metamorphic assemblage formed in the presence CO_2 during cooling, or is a reaction product associated with the very late-stage alteration of CSH. Sabine (1975) also found the petrographical relationships of the low-temperature secondary phases was difficult to establish but suggested that the scawtite in Carneal Plug was of low-temperature hydrothermal origin, probably formed before tobermorite (CSH).

4.2 ALTERATION OF CALCSILICATE NODULES FROM SCAWT HILL

The bulk mineralogy of the samples of calcsilicate nodules from Scawt Hill are summarised in Table 2. They are generally much paler than similar hornfelsed chert from the xenolithic limestone blocks found at Carneal Plug, and the matrix marble has not been so heavily metasomatised with Fe and therefore contains little or no magnetite and pyroxene mineralisation. The nodules are concentrically zoned (e.g. Plate 13), usually comprising a largely unaltered core of coarsely crystalline larnite, spurrite/paraspurrite surrounded by reaction rim of quartz and scawtite. In some cases (e.g. sample MPLM802) a central core of coarse quartz-rich material may be present, representing recrystallised chalcedonic silica that has not reacted with lime from the adjacent host limestone during metamorphism (Plate 14). Minor to trace amounts of brownmillerite and wollastonite may also be present as primary metamorphic minerals. However, wollastonite is much less abundant in the samples collected from Scawt Hill than in the samples collected from Carneal Plug (Table 2).

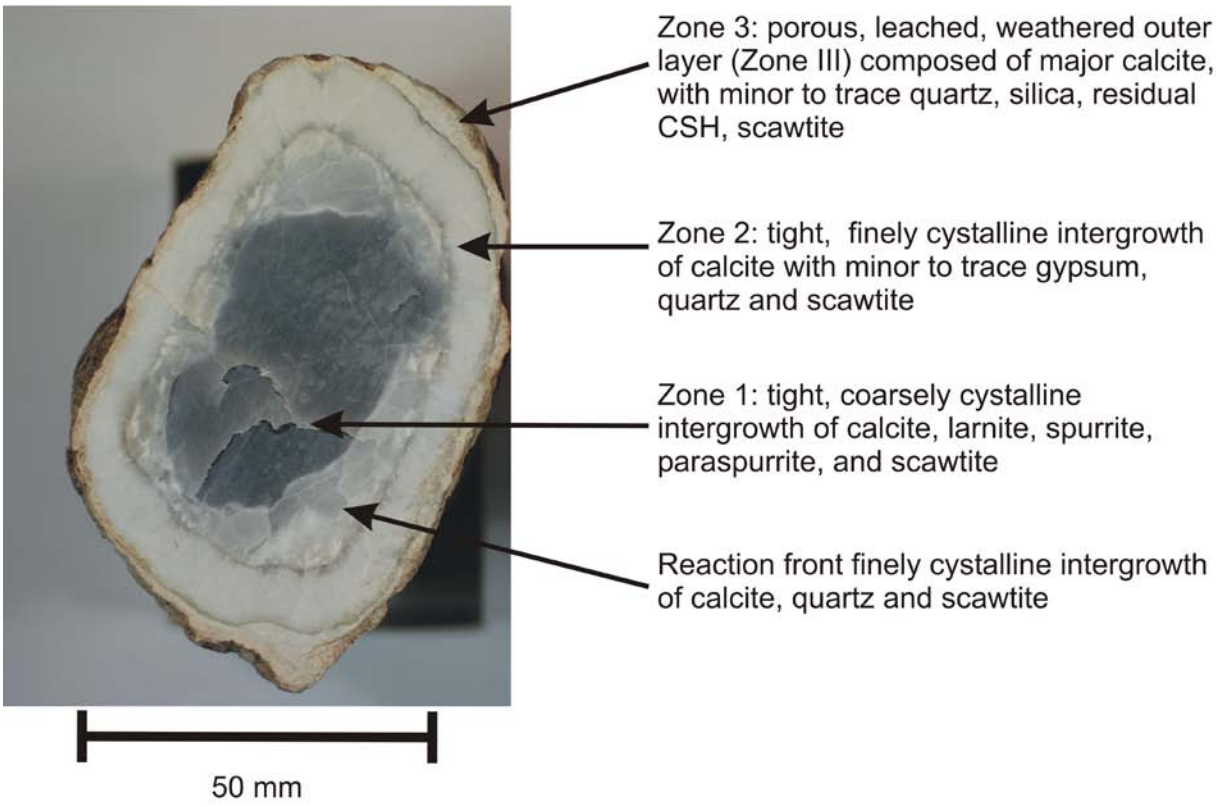

Plate 13. Section through an altered larnite-spurrite-scawtite nodule (sample MPLM796) from Scawt Hill showing concentrically banded alteration around a residual core of the original calcsilicate metamorphic rock

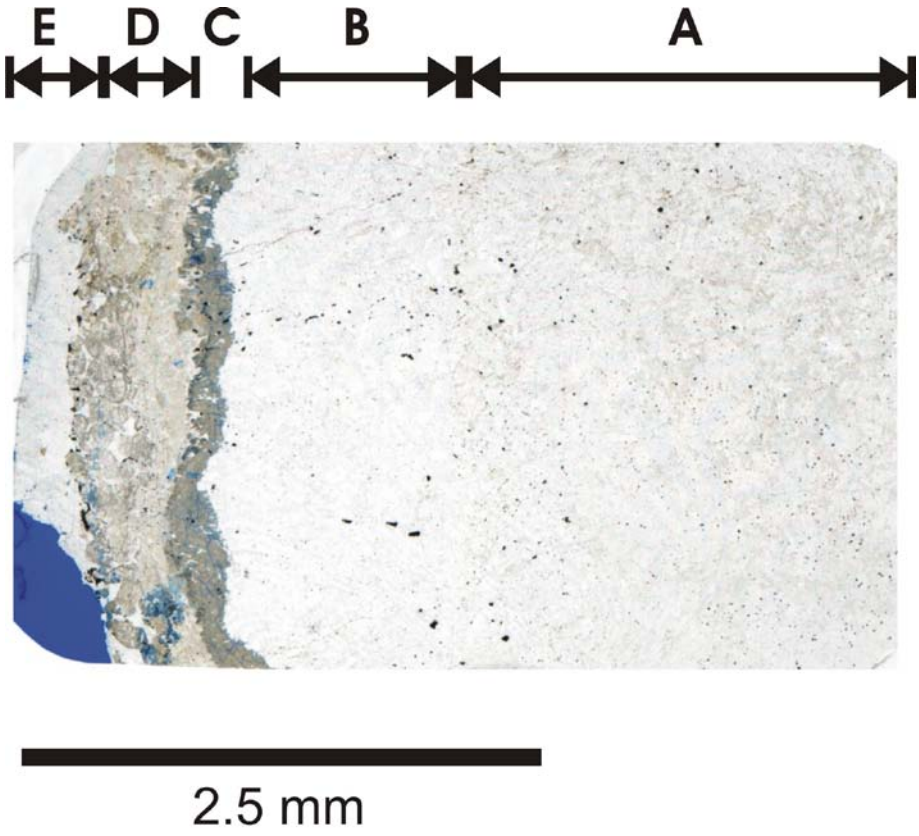

Plate 14. Transmitted light image of thin section through altered calcsilicate nodule. It shows zoned alteration: A - quartz-rich zone with minor larnite; B – larnite with minor spurrite or paraspurrite; C – Inner zone of the late-stage alteration rim, with secondary porosity highlighted by blue resin; D – zone of carbonation reaction with scawtite, amorphous silica and calcium carbonate; E – host marble. Sample MPLM802B, Scawt Hill, Northern Ireland.

As at Carneal Plug, many of the nodules display buff-coloured leached, microporous outer margins. XRD analysis shows that this leached rim is composed largely of major quartz and calcite, with minor to trace hydroxylapatite, scawtite and tobermorite. Traces of brownmillerite may still remain. In this section, the nodules can be seen to display hydration of larnite to CSH gel. Much of this CSH gel appears to be optically isotropic and may be amorphous, although in part it must also contain more crystalline tobermorite, which is detected in the XRD data. The larnite hydration to CSH is present largely towards the rim of the nodules, beneath the outer scawtite and quartz-rich band (e.g. Plate 14). The petrographical relationship between scawtite and other minerals is clearer in the samples from Scawt Hill than in Carneal Plug. The scawtite appears to be an early carbonate mineral closely associated with larnite, and predates the hydration of the larnite to CSH. It may be intergrown with larnite but appears to form a reaction band between the larnite and the host marble. In more altered regions of the nodules, the larnite may be seen to be hydrated to CSH, which fills interstitially between a skeletal framework of residual scawtite.

The secondary CSH rims are often highly microporous, and contain microcrystalline calcium carbonate which has locally nucleated within, and replaced, patches of the CSH gel (cf. also observations from Carneal Plug in Section 4.1). As in the Carneal Plus samples, the samples from Scawt Hill also display the formation of secondary microporosity closely associated with the late-stage alteration of CSH to calcium carbonates. This is best seen in sample MPLM799, which represented a nodule exposed to weathering on an in situ rock face on Scawt Hill. The larnite core of this nodule had been largely dissolved out, leaving the residual altered hydrated and carbonated rim lining the dissolution cavity. The altered rims consists mainly of calcite,

with minor hydroxylapatite (probably residual primary metamorphic apatite – cf. the occurrence of the silicoapatite mineral – ellestadite - reported previously from Scawt Hill hornfelsed cherts by Milodowski et al., 1989). BSEM-EDXA reveals that non-crystalline (with respect to XRD) CSH gel is also present in these rims. This is extensively replaced by microcrystalline calcite (Plate 15). Fine secondary silica gel is also present and finely admixed with the calcite, and probably in part corresponds to the quartz detected by XRD. The fine silica appears to be derived as a by-product of the carbonation reaction of the CSH. Abundant microporosity is present in this carbonated reaction band, and appears to have been created partly through leaching of the CSH gel and partly as a result of shrinkage of the CSH gel on its replacement by microgranular calcite.

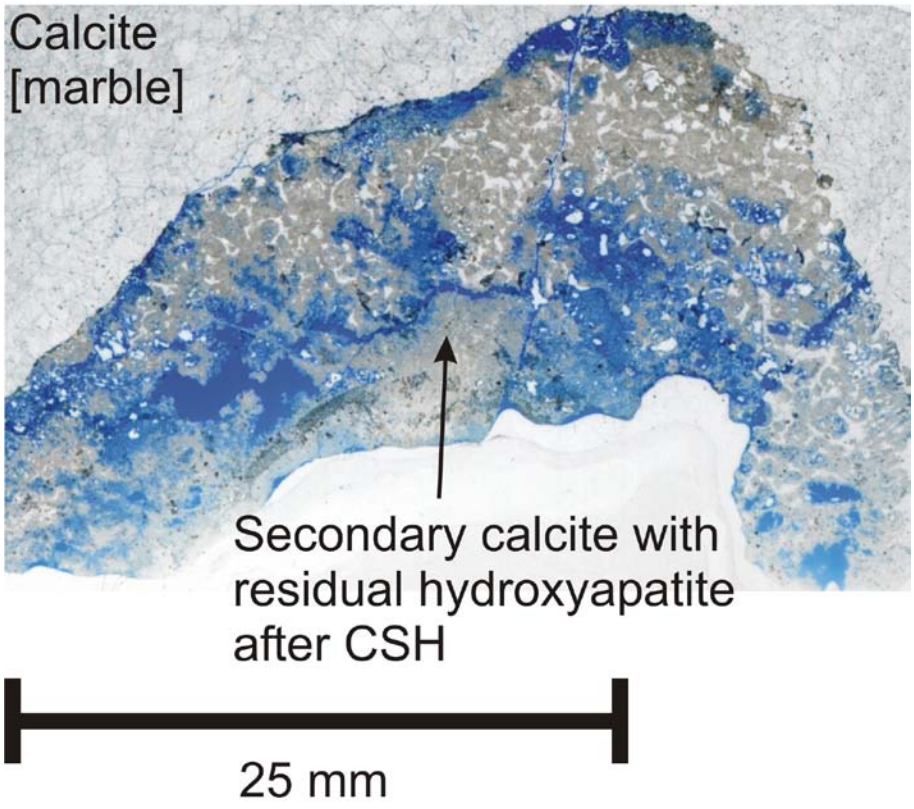

Plate 15. Transmitted light photomicrograph through the partially carbonated CSH hydration rim of an in tensely hydrated and altered larnite nodule. Fine grained grey calcite replaces the CSH gel. The alteration is highly microporous due to dissolution of CSH and shrinkage of CSH gel on carbonation. Sample MPLM799, Scawt Hill.

5 Discussion and conclusions

5.1 HYDRATION AND CARBONATION REACTIONS IN NATURAL CSH PHASES

Naturally occurring calcium silicates, calcium aluminosilicate, and CSH minerals and gels, analogous to those found in Portland cement clinkers and hydrated Portland cements, have been studied within the hornfelsed cherty Ulster White Limestone Formation (Chalk), in the narrow contact metamorphic aureoles developed around small Tertiary diorite intrusions (plugs) in County Antrim, Northern Ireland. The contact metamorphic aureoles of four Tertiary plugs were examined: Carneal Plug, Scawt Hill, Ballycraigy Plug and Ballygalley Plug. Only Carneal Plug and Scawt Hill furnished suitable natural analogue materials for this study.

Larnite, bredigite, spurrite and paraspurrite were formed by thermal metamorphism of chert concretions within the limestone. Subsequently, interaction with groundwater has hydrated the primary metamorphic assemblage (principally larnite and spurrite/paraspurrite) form xonotlite, tobermorite, and CSH gels. Traces of ettringite and gypsum were also identified. Two stages of hydration are recognised:

1. Early hydrothermal alteration under moderate temperature conditions, associated with retrograde metamorphism (i.e. cooling of the intrusion). Phases such as xonotlite are believed to have formed during this early hydrothermal stage of alteration (Sabine, 1975).
2. Late-stage hydration associated with the hydration of larnite and the formation of tobermorite and CSH gel. Sabine (1975) considered this alteration to have occurred at low temperatures (<100 °C for CSH gel and probably <160 °C for tobermorite) in the waning stages of the Tertiary hydrothermal system associated with the emplacement of the dolerite plugs. However, it is also just as likely that this low-temperature alteration could have occurred by interaction with normal low temperature background groundwater at any time since hydrothermal activity ceased, and could be ongoing at the present day. This has been observed in the Maqarin Natural Analogue Site in Jordan, where active hydration of larnite to CSH gels and tobermorite is occurring at the present-day at low-temperature (<15-20 °C) groundwater (Alexander, 1992; Linklater, 1998; Smellie, 1998; Milodowski et al., 2001).

The larnite and CSH reaction products have also interacted with CO_2 or dissolved HCO_3^- to produce secondary carbonate minerals. Carbonation reactions occurred in at least two stages:

1. Early reaction of CO_2 with larnite formed the complex hydrous calcium silicate carbonate mineral scawtite. The relationship between scawtite and late-stage CSH mineral formation is unclear in the samples examined from Carneal Plug. However, observations on samples from Scawt Hill indicate that scawtite largely formed as a discrete reaction zone at the interface between the larnite cores and the marble host rock. The mineral fabric suggests that scawtite formed prior to the hydration of larnite to tobermorite or CSH. Sabine (1975), referring to early experimental studies on scawtite stability (Buckner et al., 1960; Harker, 1965), suggested that scawtite probably formed between 225-320 °C under high partial pressures of CO_2 prevailing during retrograde metamorphism.
2. Late-stage replacement of secondary tobermorite and CSH gel by microcrystalline calcium carbonate. The calcium carbonate is dominated by calcite but vaterite and aragonite are also present. Vaterite has been identified previously from the Ballycraigy Plug, also in association with the hydration of larnite to tobermorite and CSH gel (McConnell, 1960). Ankerite was also identified as trace mineral in strongly metasomatised larnite-bearing rock from Carneal Plug.

Late-stage carbonation and replacement of CSH and tobermorite by calcium carbonate is closely associated with the progressive loss of Ca from the CSH compound, and ultimately in the formation of residual secondary silica gel or fine grained quartz. Whilst the hydration of larnite to CSH in these natural materials appears to be isovolumetric, the carbonation of the natural CSH gel and tobermorite is associated with significant volume reduction. This manifests itself in shrinkage and microfracturing of the residual CSH gel. Shrinkage and microfracturing, together with dissolution and leaching of the CSH phases has created significant secondary porosity in these rocks.

5.2 TIMESCALES OF THE LATE STAGE CARBONATION ALTERATION

Late-stage carbonation and alteration of the CSH hydration products of larnite at Scawt Hill and Carneal Plug may have occurred by either:

1. Interaction with dissolved HCO_3^- in groundwater within the saturated zone prior to uplift and exposure;
2. Interaction with atmospheric CO_2 or HCO_3^- in rainwater on exposure to aerial weathering.

At Scawt Hill the larnite nodules have been extensively leached, and the CSH rims largely replaced by secondary calcium carbonate and silica/quartz. In contrast, larnite nodules which were recovered by breaking open blocks of marble, and which had not been exposed to surface weathering showed on minor late-stage carbonation of CSH rims. This implies that carbonation is strongly influenced by exposure to weathering, atmospheric CO_2 and/or carbonic acid in rainwater. The contact metamorphic rocks observed on the southeastern rock faces of Scawt Hill have probably been exposed as a result of large landslips that affect the steep eastern margin of the Antrim Plateau, including Scawt Hill (cf. Geological Survey of Northern Ireland, 2001). These major landslips are most likely to have occurred shortly after the retreat of ice cover at the end of the last glacial maximum (24,000 to 20,000 years BP), when the ice support was lost (Mitchell, 2004). This would suggest that the observed carbonation and leaching reactions at the Scawt Hill site could have been ongoing since this time.

At Carneal Plug, the carbonation and leaching of larnite and its associated secondary CSH hydration products have been observed in material exposed in the degraded walls of a small quarry working on the western side of the plug. The CSH phases have been exposed to atmospheric CO_2 and rainwater since these faces were last worked. The age of the quarry is not known but it seems likely that it was probably worked during the last 100-200 years to produce local stone for the construction of field boundary walls. However, the presence of euhedral secondary calcite crystals lining the surfaces of fractures within the carbonated larnite nodules might indicate that the calcite crystals grew within water-saturated pores (cf. Milodowski et al., 1998) - i.e. when the rock was below the groundwater table. This would imply that carbonation of nodules may be much older.

5.3 IMPLICATIONS OF CO_2 INTERACTION WITH WELL CEMENTS

The carbonation of these natural CSH materials has clearly occurred under different conditions to those anticipated for supercritical CO_2 storage within a deep saline aquifer or depleted hydrocarbon reservoir. The natural CSH minerals will not have reacted with supercritical CO_2 at high concentration. Instead, carbonation occurred under relatively low CO_2 concentration, either by direct interaction with atmospheric CO_2 during exposure and weathering, or by interaction with HCO_3^- dissolved in dilute shallow groundwaters. For example, it is estimated that emplacement of Carneal Plug (and similar plugs like Scawt Hill) and the observed contact metamorphism of the Ulster White Limestone occurred at <700 m depth. Late-stage hydration and alteration of the contact metamorphic assemblage has probably occurred at shallower depths,

following significant post-Tertiary and Quaternary uplift and erosion which affected the region (cf. Sabine, 1975; Mitchell, 2004).

Despite these differences, the observations from Scawt Hill and Carneal Plug may provide an insight into some aspects of the interaction of CO_2 with well cements. Natural CSH gel from Scawt Hill Carneal Plug is very similar to the CSH gel encountered in Portland type cement, and has reacted with CO_2 to form secondary calcium carbonates and silica. Calcite is the dominant secondary calcium carbonate mineral but vaterite and aragonite are also formed. The carbonation produces reduction in volume, accompanied by shrinkage and microfracturing of the residual poorly crystalline CSH gel and its silica-rich alteration product. This has created significant secondary porosity in the altered material. Although some secondary calcium carbonate reaction products may partially mineralise the fractures, they do not seal the fractures completely.

Although these natural system observations are not analogous to cement-CO_2 interaction under supercritical conditions, they may provide an analogue for interaction between well cement and formation waters containing dissolved CO_2 distal to the point of injection.

References

ALEXANDER, W.R. (EDITOR). 1992. A natural analogue study of the Maqarin hyperalkaline groundwaters. I Source term description and thermodynamic testing, *Nagra Technical Report*, **91-10**.

ALEXANDER, W.R., ARCILLA, C.A., MCKINLEY, I.G., KAWAMURA, H., TAKAHASHI, Y., AOKI K. AND MIYOSHI S. 2008a. A new natural analogue study of the interaction of low-alkali cement leachates and the bentonite buffer. *Scientific Basis for Nuclear Waste Management*, **XXXI**, 493-500.

ALEXANDER, W.R., MCKINLEY, I. GARCILLA, C.A., TAKAHASHI, Y. KAWAMURA, H. NAMAKWA M. AND AOKI, K. 2008b Hyperalkaline Natural Analogue Potential in the Philippines. *Proceedings of the. 2nd East Asia Forum on Radwaste Management (EAFORM) Conference, 20-23 October 2008, Tokyo, Japan*.

ALEXANDER, W.R. AND MILODOWSKI, A.E. (EDITORS). 2009. Cyprus Natural Analogue Project (CNAP): Phase II Final Report. *Posiva Working Report*, Posiva, Olkiluoto, Finland (in press)

ANRAKU, S., MORIMOTO, K., SATO, T. AND YONEDA, T. 2009 (in press). Formation of Secondary Minerals and Uptake of Various Anions Under Naturally-Occurring Hyperalkaline Conditions in Oman. *Proceedings of the 12th International Conference on Environmental Remediation and Radioactive Waste Management, ICEM2009, 11-15 October, Liverpool, UK.* ASME, New York.

BENDER, F. 1968. *Geologie von Jordanien – Beträge zur rehgionalen Geoloie der Erde*. Gebrüder Bornträger, Berlin.

BENTOR, Y.K., GROSS, S. AND HELLER, I. 1963a. Some unusual minerals from the 'Mottled Zone' complex, Israel. *American Mineralogist*, **48**, 924-930.

BENTOR, Y.K., GROSS, S. AND HELLER, I. 1963b. High temperature minerals in non-metamorphosed sediments. *Nature*, **199**, 478.

BENTOR, Y.K., GROSS, S. AND KOLODNY, Y. 1972. New evidence on the origin of high temperature assemblage of the 'Mottled Zone' Israel. *Proceedings of the 24th International Geological Congress (Montreal, Canada),* **Section 2**, 265-275.

BENTOR, Y.K. AND KASTENER, M. 1976. Combustion metamorphism in Southern California. *Science*, **193**, 486.

BUCKNER, D.A., ROY, D.M. AND ROY, R. 1960. Studies in the system CaO-Al_2O_3-SiO_2-H_2O. II The system $CaSiO_3$-H_2O. *American Journal of Science*, **258**, 132-147.

BURNHAM, C.W. 1959. Contact metamorphism of magnesian limestones at Crestmore, California. *Bulletin of the Geological Society of America*, **70**, 879-920.

EMELEUS, .C.H. AND PRESTON, J. 1969. *Field Excursion Guide: The Tertiary Volcanic Rocks of Ireland.* Belfast.

GLASSER, F.P. 2001. Mineralogical aspects of cement in radioactive waste disposal. Mineralogical magazine, 65(5), 621-633.

GRIFFITH, A.E. AND WILSON, H.E. 1982. *Geology of the country around Carrickfergus and Bangor. Memoir for One-Inch Geological Sheet 29 (2nd Edition)*. Geological Survey of Northern Ireland, Institute of Geological Sciences, Belfast, HMSO.

HILLIER, S., SUZUKI, K. AND COTTER-HOWELLS, J. 2001. Quantitative determination of Cerussite (lead carbonate) by X-ray powder diffraction and inferences for lead speciation and transport in stream sediments from a former lead mining area of Scotland. *Applied Geochemistry*, 16, 597-608.

IPCC. 1990. Scientific Assessment of Climate Change. *Working Group 1 Report of the Intergovernmental Panel on Climate Change*, WNO, Geneva. World Wide Web Address: http://www.ipcc.ch/ipccreports/assessments-reports.htm.

IPCC. 2005. Carbon Dioxide Capture and Storage. *Working Group 3 report of the Intergovernmental Panel on Climate Change* (Editors: METZ, B., DAVIDSON, O., CONINCK, H. DE, LOOS, M. AND MEYER, L.), Cambridge University Press, New York, 431pp.

IPCC. 2007. *Forth Assessment Report: Climate Change*. Published by the IPCC. World Wide Web Address: http://www.ipcc.ch/ipccreports/assessments-reports.htm.

GEOLOGICAL SURVEY OF NORTHERN IRELAND. 2001. Ballymena. Northern Ireland Sheet 20, Solid and Drift Geology. 1:50 000. British Geological Survey, Keyworth, Nottingham.

GOLDSTEIN, J.I., NEWBURY, D.E., ECHLIN, P., JOY, D.C., FIORI, C. AND LIFSHIN, E. 1981. *Scanning Electron Microscopy and X-Ray Microanalysis*. Plenum Press, New York.

GROSS, S. 1977. The mineralogy of the Hatrurim Formation, Israel. *Bulletin of the Geological Survey of Israel*, **70**, 80pp.

HARKER, R.I. 1965. Scawtite and its synthesis. *Mineralogical Magazine*, **34**, 232-236.

KOLODNY, Y. 1970. Natural cement factory: a geological story. In: SKALNY, J., (Editor) *Proceedings of the Conference on Cement Production and Use, Franklin Pierce College, Ridge, New Hampshire, 24-29 June 1979.*

KHOURY, H.N. AND NASSIR, S. 1982. High temperature mineralization in the bituminous limestone in Maqarin area – north Jordan. *Neus Jahbuch für Mineralogie Abhandlungen*, **144**, 197-213.

LINKLATER, C.M. (EDITOR). 1998. A natural analogue study of cement-buffered, hyperalkaline groundwaters and their interaction with a repository host rock, phase II, *UK Nirex Ltd. Science Report*, **S/98/003**.

MCCONNELL, J.D.C. 1954. The hydrated calcium silicates riversideite, tobermorite and plombierite. *Mineralogical Magazine*, **30**, 293-305.

MCCONNELL, J.D.C. 1955. The hydration of larnite (β-Ca_2SiO_4) and bredigite (α_1-Ca_2SiO_4), and the properties of the resulting gelatinous mineral plombierite. *Mineralogical Magazine*, **30**, 672-680.

MCCONNELL. 1960. J.D.C. Vaterite from Ballycraigy, Larne, Northern Ireland. *Mineralogical Magazine*, **32**, 535-545.

NEAL, C. AND STANGER, G. 1984. Calcium and magnesium hydroxide precipitation from alkaline groundwaters in Oman, and their significance to the processes of serpentinisation. *Mineralogical Magazine*, **48**, 237-241.

MILODOWSKI, A.E., NANCARROW, P.H.A. AND SPIRO, B., 1989. A mineralogical and stable isotope study of natural analogues of Ordinary Portland Cement (OPC) and CaO-SiO_2-H_2O (CSH) compounds. *United Kingdom Nirex Safety Studies Report*, **NSS/R240**.

MILODOWSKI, A.E., GILLESPIE, M.R., NADEN, J., FORTEY, N.J., SHEPHERD, T.J., PEARCE, J.M. AND METCALFE, R. 1998 The petrology and paragenesis of fracture mineralisation in the Sellafield area, west Cumbria. *Proceedings of the Yorkshire Geological Society*, **52**, 215-241.

MILODOWSKI, A.E., HYSLOP, E.K., KHOURY, H.N., HUGHES, C.R., MÄDER, U.K., GRIFFAULT, L. AND TROTIGNON, L. 2001. Mineralogical alteration by hyperalkaline groundwater in northern Jordan. In: CIDU, R. (EDITOR) *Proceedings of the Tenth International Symposium on Water-Rock Interaction WRI-10, Villasimus, Italy, 10-15 July 2001*, 1347-1350.

MILODOWSKI, A.E., CONSTANTINUOU, C.A., ALEXANDER, W.R., RIGAS, M., TWEED, C.J., SELLIN, P., KORKEAKOSKI, P., KEMP, S.J. AND RUSHTON, J.C. 2009 (in press). Reaction of bentonite in low alkali cement leachates: preliminary results from the Cyprus Natural Analogue Project (CNAP). *Proceedings of the 12th International Conference on Environmental Remediation and Radioactive Waste Management, ICEM2009, 11-15 October, Liverpool, UK.* ASME, New York.

MITCHELL, W.I. 2004. *The Geology of Northern Ireland*. Geological Survey of Northern Ireland, Belfast.

PITTY, A.F. (EDITOR). 2009 (in press). A natural analogue study of cement buffered, hyperalkaline groundwaters and their interaction with a repository host rock IV: an examination of the Khushaym Matruk (central Jordan) and Maqarin (northern Jordan) sites. *NDA-RWMD Technical Report*, Nuclear Decommissioning Authority, UK (in press).

RCEP. 2000. *Energy - The Changing Climate*. Twenty-second Report of the Royal Commission on Environmental Pollution, **Cm 4749**, 292pp.

ROCHELLE, C.A., MILODOWSKI, A.E., SHI J.-Q., MUNOZ-MENDEZ, G., JACQUEMET, N. & LECOLIER, E. 2008. A review of the potential impact of CO_2 on the integrity of well infrastructure for underground CO_2 storage. *British Geological Survey Commissioned Report*, **CR/07/204**. 76pp.

ROCHELLE, C.A., MILODOWSKI, A.E., LACINSKA, A., RICHARDSON, C., SHAW, R., TAYLOR, H., WAGNER, D., BATEMAN, K., LÉCOLIER, E., FERRER, N., LAMY, F., JACQUEMET, N., SHI, JI-Q., DURUCAN, S. AND SYED, A.S. 2009. JRAP-14: *Reactions between CO_2 and borehole infrastructure; Report on laboratory experiments and modelling*. Report for JRAP-14/3, European Commission Contract No. SES6-CT-2004-502816., 138pp.

SABINE, P.A. 1975. Metamorphic processes at high temperatures and low pressure: the Petrogenesis of the metasomatized and assimilated rocks of Carneal Plug, Co. Antrim. *Philosophical Transactions of the Royal Society, London*, **280(A)**, 225-265.

SABINE, P.A., BECKINSALE, R.D., EVANS, J.D. AND WALSH, J.N. 1982. Geochemical and strontium isotope studies of reactions between basic magma, Chalk, and flint, and the role of groundwater, in the Carneal Plug, Co. Antrim, Northern Ireland. *Journal of Petrology*, **23**, 427-446.

SABINE, P.A., STYLES, M.T. AND YOUNG, B.R. 1985. The nature and paragenesis of natural bredigite and associated minerals fro Carneal and Scawt Hill, Co. Antrim. *Mineralogical Magazine*, **49**, 663-670.

SMELLIE, J.A.T. (EDITOR). 1998. Maqarin natural analogue study, Phase III, *SKB Technical Report*, **TR-98-04**.

SMELLIE, J.A.T., ALEXANDER, W.R., DEGNAN, P., GRIFFAULT, L., MÄDER, U.K. AND TROTIGNON, L. 2001. The role of the Jordan natural analogue studies in the performance assessment of cementitious repositories for radioactive wastes. In: CIDU, R. (EDITOR) *Proceedings of the Tenth International Symposium on Water-Rock Interaction WRI-10, Villasimus, Italy, 10-15 July 2001*, 1391-1393.

SNYDER, R.L. AND BISH, D.L. 1989. Quantitative analysis. In: Bish, D.L., Post, J.E. (Eds), *Modern Powder Diffraction, Reviews in Mineralogy*, Volume 20, Mineralogical Society of America, USA, pp. 101-144 (Chapter 5).

STANGER, G. AND NEAL, C. 1984. A new occurrence of suolinite from Oman. *Mineralogical Magazine*, **48**, 143-146.

TILLEY, C.E. 1929. On larnite (calcium orthosilicate, a new mineral) and its associated minerals from the limestone contact-zone of Scawt Hill, Co. Antrim. *Mineralogical Magazine*, **22**, 77-86.

TILLEY, C.E. 1930. Scawtite, a new mineral from Scawt Hill, Co. Antrim. *Mineralogical Magazine*, **22**, 222-224.

TILLEY, C.E. 1933. Portlandite, a new mineral from Scawt Hill, Co. Antrim. *Mineralogical Magazine*, **23**, 419-420.

TILLEY, C.E. AND ALDERMAN, A.R. 1934. Progressive metamorphism in the flint nodules of the Scawt Hill contact-zone. *Mineralogical Magazine*, **23**, 513-518.

TILLEY, C.E. AND HARWOOD, H.F. 1931. The dolerite-chalk contact of Scawt Hill, Co. Antrim. The production of basic alkali-rocks by the assimilation of limestone by basaltic magma. *Mineralogical Magazine*, **22**, 439-468.

TILLEY, C.E. AND VINCENT, H.C.G. 1948. The occurrence of an orthorhombic high-temperature form of Ca_2SiO_4 (bredigite) in the Scawt Hill contact-zone and as a constituent of slags. *Mineralogical Magazine*, **28**, 255-271